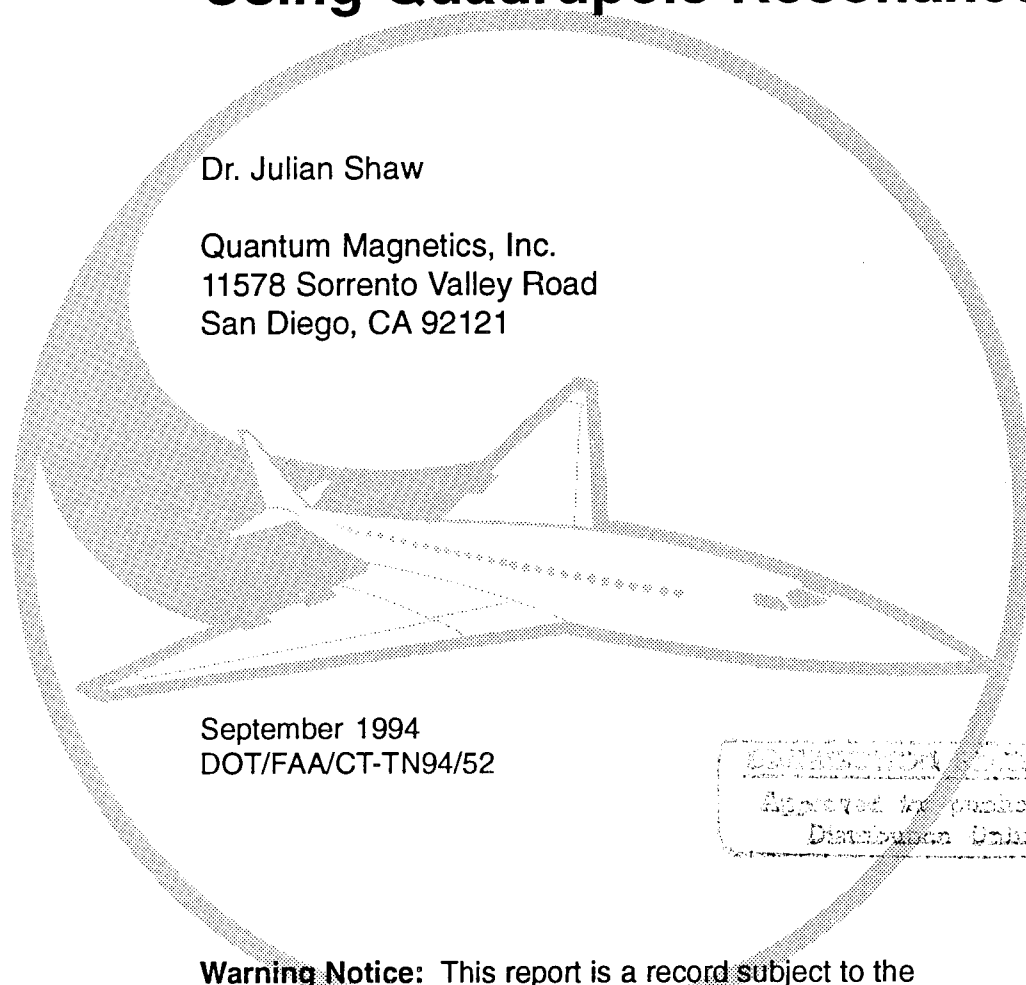


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Detectability of Explosives Using Quadrupole Resonance

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September 1994
DOT/FAA/CT-TN94/52

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Technical Report Documentation Page

1. Report No. DOT/FAA/CT-TN94/52		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle DETECTABILITY OF EXPLOSIVES USING QUADRUPOLE RESONANCE				5. Report Date SEPTEMBER 1994	
				6. Performing Organization Code	
7. Author(s) Dr. Julian Shaw				8. Performing Organization Report No.	
9. Performing Organization Name and Address Quantum Magnetics, Inc. 11578 Sorrento Valley Road San Diego, CA 92121				10. Work Unit No. (TRAIS)	
				11. Contract or Grant No. DTFA03-94-C-00046	
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Office of Civil Aviation Security 800 Independence Ave., S.W. Washington, DC 20591				13. Type of Report and Period Covered Technical Note Aug-Sep 1994	
				14. Sponsoring Agency Code ACS-1	
15. Supplementary Notes Dr. Ronald A. Krauss, Systems Development Division (ACA-600), Aviation Security Research and Development Service, was the Contracting Officer's Technical Representative (COTR) for the subject effort.					
16. Abstract The purpose of this report is to summarize the currently available information on (1) quadrupole resonance (QR) characteristics of explosive materials and their accessibility to QR detection , and (2) the potential of detecting explosives in explosive mixtures by using the quadrupole resonance signals of other materials commonly found as additives, such as plasticizers, binders and stabilizers.					
17. Key Words Nuclear Quadrupole Resonance, NQR Explosives Scanner			18. Distribution Statement <u>Approved for U.S. Government Use Only.</u> This report is a record subject to the provisions of 14 CFR 191.1 et seq. Release of information contained herein is prohibited without the express written approval of the Assistant Administrator for Civil Aviation Security, ACS-1, or his designee.		
19. Security Classif. (of this report) FOR OFFICIAL USE ONLY	20. Security Classif. (of this page) UNCLASSIFIED		21. No. of Pages 21	22. Price	

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List of Abbreviations and Symbols

NRL:	Naval Research Laboratory, Washington, D.C.
QM:	Quantum Magnetics, Inc.
QR, NQR:	Quadrupole Resonance, Nuclear Quadrupole Resonance
NMR:	Nuclear Magnetic Resonance
SSFP:	Steady State Free Precession
SORC:	Strong Off-Resonance Comb
RF:	Radiofrequency
HTS:	High Temperature Superconductor
LTS:	Low Temperature Superconductor
PAPS:	Phase Alternated Pulse Sequence
NPAPS:	Non-Phase Alternated Pulse Sequence
SQUID:	Superconducting Quantum Interference Device
SNR:	Signal to Noise Ratio
ν_+ :	Frequency associated with nuclear quadrupole resonance transition
ν_- :	Frequency associated with nuclear quadrupole resonance transition
ν_0 :	Frequency associated with nuclear quadrupole resonance transition

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Executive Summary

Recent advances in the field of quadrupole resonance have given rise to increased interest in quadrupole resonance (QR) as a technique for detecting explosives hidden in airline baggage. This report summarizes the explosive materials detectable by QR, their characteristic responses, and their relative detectability compared to RDX using currently available technology. Suggestions are also made on technological advances currently taking place which may significantly increase the number of explosives accessible to QR detection, and also enhance the sensitivity of QR detection.

1 Introduction

New information about the quadrupole resonance characteristics of explosive materials, new experimental techniques, and instrumental advances has given rise to increased interest in quadrupole resonance (QR) as a technique for detecting explosives hidden in airline baggage.

This report summarizes the explosive materials detectable by QR and their characteristic responses. The information presented in this report was obtained from a variety of sources including:

- (1) Literature surveys of the field of quadrupole resonance and explosives detection carried out over the past three years by the contractor.
- (2) Unpublished information and communications.
- (3) Unpublished results of tests carried out at Quantum Magnetics on a QR package scanner.
- (4) Analyses carried out on the relative sensitivities of various QR detection technologies.

An introduction to QR is followed by a summary of the application of QR to explosives detection and a comparison of detection technologies. Details of the quadrupole characteristics of each material are presented and detection limits discussed. Finally, a summary and recommendations are presented.

2 Background to Quadrupole Resonance

As an analytical tool, QR is a branch of radio frequency spectroscopy that exploits the inherent electrical properties of atomic nuclei. Nuclei with nonspherical electric charge distributions possess electric quadrupole moments. Quadrupole resonance arises from the interaction of the nuclear quadrupole moment of the nucleus with the local electric field gradient produced by the surrounding atomic environment.

When an atomic quadrupolar nucleus is within an electric field gradient, variations in the local field associated with the field gradient affect different parts of the nucleus in different ways. The combined forces of these fields cause the quadrupole to experience a torque, and thus precess about the electric field gradient. Precessional motion generates an oscillating nuclear magnetic moment. An externally applied radio frequency magnetic field pulse in phase with the quadrupole's precessional frequency can momentarily tip the orientation of the nucleus. The pulse causes the quadrupole to generate a signal, known as the Free Induction Decay (FID) [1][2]. A pick-up coil detects the signal, which is subsequently amplified by a sensitive receiver to measure its characteristics.

A significant characteristic of a QR response is its precessional frequency. Two independent factors determine a nucleus' precessional frequency: the quadrupolar nucleus under study and its local crystalline environment. The electric quadrupole moment of the nucleus determines frequency, which is related to the electric charge and distribution of the nuclei. The frequency is also governed by the principal components of local (crystal) electric field experienced by the nucleus. Thus, there may be one or more characteristic QR frequencies for each material containing quadrupolar nuclei.

A second distinguishing characteristic, relaxation time, is a measurement of the nuclear spins' rates of return to their equilibrium states following disturbance by an RF field. Relaxation times are compound-, temperature-, and pressure-specific, and determine the frequency repetition rate of RF pulse sequences appropriate for detecting the QR signals. These relaxation times can be as short as a few hundred microseconds or as long as several seconds.

One of the main problems associated with the detection of QR signals is the low signal intensity. A technique developed to enhance the available signal relative to the background noise within a given time is a spin refocusing scheme known as steady state free precession (SSFP). This technique was developed for use in nuclear magnetic resonance experiments by Carr [3], and refers to the steady state condition that occurs when a spin system is subjected to a continuous train of RF pulses separated by a time interval τ . The advantage of using this type of sequence is the increase in the SNR within a given time period.

One variant of this technique is the Strong Off-Resonance Comb (SORC) developed by Marino et al. [4,5], in which the train of pulses has identical phase. The NRL group [6] and others [7,8] have proposed and implemented further variants in QR detection applications

3 Comparison of Detection Technologies

In the QR detection systems so far developed, the QR signature is detected using so-called "conventional" methods based on the Faraday induction effect. These conventional methods are inherently insensitive at relatively low signal frequencies. This sensitivity problem can be solved using Superconducting QUantum Interference Devices (SQUIDs). SQUIDs are the most sensitive magnetic-field detectors known, and unlike conventional detection coils, they maintain their sensitivity as the frequency decreases.

Furthermore, SQUID detectors make it possible to increase the bandwidth of the detection circuit while still maintaining high sensitivity. In contrast, conventional detectors require resonant input circuits with very high quality factors (Q's). This produces a narrow frequency response that restricts the signal bandwidth and makes multiple explosive detection difficult. SQUID detectors can help overcome such bandwidth restrictions.

In the past, the application of SQUIDs outside the laboratory has been impeded by the need for liquid helium. However, with high temperature superconducting (HTS) SQUIDs, the development of very compact, self-contained SQUID systems using reliable, inexpensive miniature closed-cycle refrigerators is possible. Reliable, reasonably priced refrigerators are now available for SQUIDs based on low temperature superconductors (LTS).

Conventional NMR detection coils are intrinsically inefficient at low frequencies. These detectors measure the voltage induced in a copper coil by the oscillating nuclear magnetic field. This induced voltage is proportional to frequency, while the Johnson noise voltage in the coil is only minimally dependent on frequency. Evaluated in terms of magnetic-field amplitude, the noise in the detection coil is nearly proportional to the inverse of the frequency. SQUIDs, on the other hand, detect the amplitude of the magnetic field rather than its rate of change. Their sensitivity remains essentially constant as the frequency is reduced. As a result, SQUIDs are much more sensitive at low QR frequencies than conventional QR detection systems.

There is no direct way of comparing the conventional detection method to SQUID-based methods, as they measure different parameters. Conventional QR detectors measure voltage and SQUID detectors measure flux. However, it is possible to compare the relative QR signal-to-noise ratio, the voltage-to-voltage noise for conventional QR, and the flux-to-flux noise for SQUID detection. Figure 1 shows the relative sensitivity of conventional (Faraday) detection devices compared to two potential SQUID-based devices for a 240 liter detection volume. The diagonal line is a measure of QR sensitivity, using a conventional copper coil and preamplifier, as a function of frequency. The upper horizontal line is a measure of the QR detection sensitivity of an untuned commercial LTS SQUID sensor. The lower horizontal line is a measure of the QR detection sensitivity of an untuned, low noise LTS SQUID sensor. As can be seen from the figures, the untuned commercial LTS SQUID sensor becomes more sensitive below

800 KHz for a 240 liter coil. For the untuned low noise LTS SQUID, sensitivity is better than conventional QR detectors at frequencies below 8 MHz.

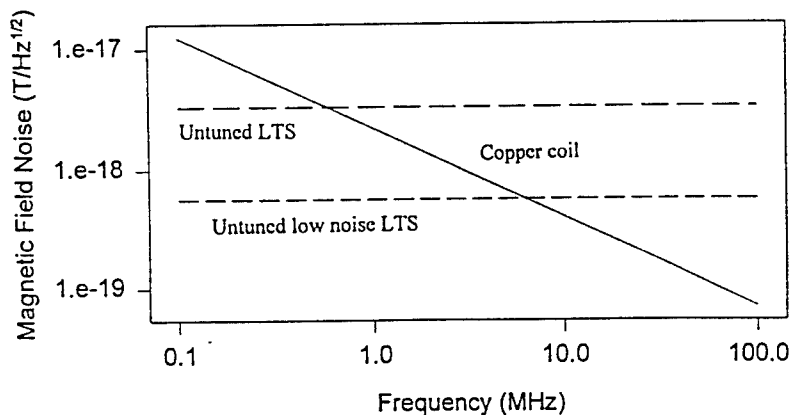


FIGURE 1. Comparison of Relative QR Detection Sensitivity Using Conventional and SQUID-based Detectors for 240 Liter Volume

SQUIDs also have advantages in bandwidth detection capabilities as well as pure sensitivity. In conventional QR detectors, the pickup coil is incorporated into a resonant circuit in order to match its impedance to that of a semiconductor-based preamplifier. The resonant circuit needs to have a high Q to minimize the contribution of the preamplifier to the noise in the QR measurement. However, a high-Q circuit has a very narrow bandwidth, and although this can be useful in single frequency (single explosive) detection, it presents some difficulties when multiple frequency (multiple explosive) detection is desired. For a dual-explosive scanner of minimum size a double-tuned coil will be required, and a compromise will have to be made between optimizing at two separate frequencies. This will lead to a reduction in optimum sensitivity at both frequencies, which may be greater than 50%. With SQUID-based detection, however, the inherently broad band nature of the detector means that a tuned circuit may not necessarily be required, which in turn implies no compromise in detection at multiple frequencies. Recent work by Clarke's group in Berkeley [9] and at QM [10], has confirmed that SQUID detection of QR signals is feasible, even in the 10-100 KHz range. Moreover, three separate frequencies were detected simultaneously.

4 Quadrupole Resonance Detection of Explosives

There are a number of quadrupolar nuclei present in explosive materials: nitrogen (^{14}N), chlorine (^{35}Cl , ^{37}Cl), oxygen (^{17}O) and potassium (^{39}K). The most commonly occurring, easily accessible quadrupolar nuclei in explosive materials are nitrogen (^{14}N), and chlorine (^{35}Cl and ^{37}Cl). The most studied quadrupole nucleus for explosives detection is nitrogen.

There are three main explosive materials that have been extensively studied and characterized using quadrupole resonance: RDX, HMX and TNT. PETN, ammonium perchlorate, potassium nitrate, nitrocellulose and ammonium nitrate have also been studied, although less extensively and less successfully. All these explosives contain a significant amount of nitrogen. The nitrogen-14 quadrupolar nuclei have been found to provide the most useful QR response for explosive detection applications.

There are three parameters that are important in selecting a QR transition as the characteristic signature for explosives detection applications: (1) the sensitivity of detection must be sufficient; (2) the relaxation times of the transition need to be suitable for the SSFP method of detection; and (3) the frequency shift of the QR transition with temperature must be small. In some of the explosives studied by QR there has been no choice; in others (such as RDX) a combination of these factors has been employed to determine the most effective transition to use.

This report summarizes the currently available information on the quadrupole resonance characteristics of the following materials: RDX, HMX, TNT, potassium nitrate, ammonium nitrate, ammonium perchlorate, PETN, and nitrocellulose. QR detection of RDX has already been established in a laboratory environment. Further documentation would be superfluous. However, detection of RDX does provide a number significant guidelines for ascertaining the parameters crucial to determining the detection sensitivity of materials containing quadrupolar nuclei. For this reason, a short summary of the available information is presented. RDX will be used as a measure of relative detection sensitivity of other explosive materials.

4.1 RDX

In RDX there is one accessible quadrupolar nucleus, ^{14}N , present in two distinct environments: ring and nitrate. Hexahydro-1,3,5-trinitro-s-triazine, RDX, has been subjected to the most extensive QR studies of all the explosive materials. The most thorough experimental analysis of RDX has been carried out by Karpowicz and Brill [11], and Marino, Leonard and Connors [4].

In the work by Karpowicz and Brill, the temperature dependence of the frequency of the ring nitrogen QR transitions was studied over the temperature range 77K to 338K. The transitions occur in three groups, which correspond to the energy level transitions for a spin $I=1$ nucleus: the $\nu+$, $\nu-$ and ν_0 . Within these three groups there are also three transitions per group, which is caused by the crystallographic non-equivalence of the

three ring nitrogens. The frequencies for the $\nu+$ and $\nu-$ transitions are given in Table 1. The significance of these results is found in the choice of QR transition for explosive detection applications. In RDX, the $\nu+$ transition would yield the best detection sensitivity. The relaxation times for $\nu+$ and $\nu-$ transitions are closely similar for all transitions, and give excellent SSFP signals. However, over the temperature range of 278 K to 318 K, the $\nu+$ transition frequency for RDX changes from 5199 KHz to 5183 KHz. Given the likelihood of experiencing explosives detection environments over this kind of temperature range, this change is far from ideal. Thus, the $\nu-$ transition at 3410 KHz looks more attractive from this standpoint (3412 to 3408 KHz frequency shift over the same temperature range). This is the primary reason for choosing this transition for explosives detection applications.

In the work by Marino, Leonard and Connors [4], the problem of very rapid detection of QR signals was first addressed. This work saw the most important advance in QR explosives detection techniques: the so-called SORC (Strong Off-Resonance Comb), a variant of the SSFP method.

Later work by other groups, in particular the NRL group lead by Garroway [12], further refined both the instrumental and experimental advances made by Marino, so that QR detection of the plastic explosive RDX could become feasible in real world explosives scanning.

For QR detection purposes, RDX will be the compound against which other materials are compared.

4.2 HMX

In HMX there is one accessible quadrupolar nucleus, ^{14}N present in two distinct environments: ring and nitrate. β -Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was studied by Landers, Brill and Marino [13], and also by Marino, Leonard and Connors [4]. Although of slightly less importance as an explosive material, it is found in many mixtures of explosive materials, such as rocket fuels.

In the work by Landers, Brill and Marino, the temperature dependence of the frequency of the ring nitrogen QR transitions was studied over the temperature range 77K to 426K. As with RDX, the transitions occur in three groups which correspond to the energy level transitions for a spin $I=1$ nucleus: the $\nu+$, $\nu-$ and ν_0 . Within these three groups there are also two transitions per group, which is caused by the crystallographic non-equivalence of four ring nitrogens (two fold symmetry about an axis defined by two opposite NO_2 groups). The frequencies for the $\nu+$ and $\nu-$ are close to those observed in RDX. The significance of these frequencies and relaxation times for explosives detection applications is that the QR parameters for RDX and HMX are sufficiently close such that the simultaneous detection of both substances is relatively straightforward. However, given the current low priority of detecting HMX, the issue of simultaneous detection will be left to a future program.

The estimated detection sensitivity of HMX is shown in Table 1.

4.3 TNT

Trinitotoluene (TNT) and other analogues formed during the manufacture of TNT (such as TNB) form the second most studied explosive materials. There is one accessible quadrupolar nucleus: ^{14}N , found in the nitrate $^{14}\text{NO}_3$ environment.

The QR characteristics of TNT were first studied by Subbarao and Bray [14,15] and later by Marino, Leonard and Connors [4]. At room temperature α -TNT occurs in two crystallographic forms: orthorhombic and monoclinic. The form depends on the physical conditions of formation or recrystallization. For each of these forms there are six crystallographically or chemically inequivalent ^{14}N sites. For each site there are three transition frequencies: ν_+ , ν_- and ν_0 . These transition frequencies are centered around 875, 750 and 125 KHz, respectively. However, because of the large number of inequivalent nitrogen sites, "dilution" effects are a problem with TNT. For this reason, and because TNT is not very accessible to the SSFP sequences at room temperature, it is unlikely that TNT will be detectable by conventional QR at sensitivities required for fast throughput. The NRL group has been unsuccessful in detecting TNT at room temperature.

The estimated detection sensitivity of TNT is shown in Table 1.

4.4 Potassium Nitrate

Potassium nitrate, the major component of black powder, has two potentially-detectable quadrupolar nuclei: ^{39}K and ^{14}N . Both sets of transition frequencies have been determined by indirect detection methods using NMR single crystal rotation studies [16]. For ^{39}K , the transition frequency at room temperature is 666 KHz. For ^{14}N , the transition frequencies at room temperature are at 567 and 559 KHz for ν_+ and ν_- , respectively. This work also gives the temperature dependence of the QR transitions. For ^{14}N , the frequency decreases by about 6 KHz when the temperature increases by 30 K; for ^{39}K , the frequency decreases by about 12 KHz when the temperature increases by the same amount.

Potassium nitrate has not been directly detected by QR. An estimate of the likely detection sensitivity is shown in Table 1.

4.5 Ammonium Nitrate

^{14}N is the one QR-accessible quadrupolar nucleus present in ammonium nitrate. In AN, ^{14}N is present in two forms, ammonium ($^{14}\text{NH}_4$) and nitrate ($^{14}\text{NO}_3$). The QR transition frequencies of ammonium nitrogens tend to be lower than nitrate nitrogens.

The crystallographic phase of ammonium nitrate varies with temperature. Over the temperature range of interest in detection applications, ammonium nitrate is present in two crystallographic forms (Phase IV and III), with the transition occurring at about 303

K (300°C). Ammonium nitrate has been the subject of a number of studies that have shed light on the quadrupolar interaction. Initial studies using indirect measurement techniques (NMR/NQR double resonance) [17] gave both the $^{14}\text{NO}_3$ and the $^{14}\text{NH}_4$ resonance frequencies.

For the $^{14}\text{NO}_3$ group in Phase IV, the transition frequencies at 298 K measured using indirect detection are about 500 and 420 KHz for ν_+ and ν_- , respectively. For the $^{14}\text{NO}_3$ group in Phase III, the transition frequencies at 305 K (measured using indirect detection) only one frequency was observed at about 500 KHz, corresponding to both ν_+ and ν_- lines.

The most remarkable feature of the QR transition frequencies occurs in the ammonium group. The ^{14}N quadrupole coupling constant—and therefore transition frequencies—is the highest for any ammonium group. In Phase IV, $^{14}\text{NH}_4$ resonance frequencies are about 235, 130 and 105 KHz for ν_+ , ν_- and ν_0 , respectively. Above 300°C, when AN is in Phase III, $^{14}\text{NH}_4$ resonance frequencies change to about 105, 80, and 25 KHz. These results were obtained using indirect detection of the QR signals.

Direct QR detection of $^{14}\text{NO}_3$ in AN has been attempted at both 298 K and 77K by Marino [18]. The data obtained at 77K showed two surprisingly narrow ν_+ lines at 554.4 and 557.8 KHz. Tentative data were also reported at room temperature.

An estimate of the likely detection sensitivity is shown in Table 1.

4.6 Ammonium Perchlorate

Ammonium perchlorate has been studied using both nuclear magnetic resonance and quadrupole resonance [9,10,19]. There are three potential quadrupolar nuclei that could provide useful information for detection applications: ^{14}N , ^{35}Cl and ^{37}Cl .

For the ammonium ^{14}N , indirect measurements using NMR [19] have given a quadrupole coupling constant of 53.3 KHz at room temperature, which would give three transition frequencies at 41.9, 38.5, and 3.4 KHz for ν_+ , ν_- and ν_0 , respectively. These results have been confirmed by direct detection using a DC SQUID [9,10] at 1.5K, with transition frequencies 56.2, 38.8, and 17.4 KHz. The reported relaxation times at 1.5 K of the central transition at 38.8 KHz were 22 ms for the spin-spin relaxation time (T_1), and 63ms for the spin-lattice (T_2) relaxation times. It is likely that these times will be significantly shorter at room temperature.

For the chlorate ^{35}Cl , indirect measurements using NMR [19] have given a quadrupole coupling constant of 694.9 KHz at room temperature, which would give a single transition frequency of 379 KHz. No measurements are available on the quadrupolar relaxation times for ^{35}Cl in ammonium perchlorate. No information is available on the QR signature of ^{37}Cl .

An estimate of the likely detection sensitivity of ammonium perchlorate using conventional detection techniques is shown in Table 1.

4.7 PETN

Pentaerythritol tetranitrate (PETN) was initially investigated using QR by Marino et al. [20]. Their initial measurements showed a very low intensity signal at about 900 KHz. Later work by the NRL group confirmed this result. Work on PETN has also been carried out by Grechishkin et al. [21]. However, Grechishkin's results are inconsistent, nor do they concur with Marino's and Garroway's work. Work has also been carried out in London [22], using a double resonance technique to characterize the QR transitions of PETN. These results further substantiate the work carried out by Marino and the NRL group.

Full characterization of the QR response of PETN in explosives detection is as yet incomplete. The main problem with PETN that still needs to be addressed is in finding a method of detecting PETN to the same level as RDX. The NRL group is currently working on this issue. However, given the lower frequency of the QR transition ($\nu \sim 890 \text{ KHz}$), combined with the relatively long spin-lattice relaxation time (~ 32 seconds), it is unlikely that the sensitivity equal to that of RDX will be obtained with conventional detection techniques. If the RDX detection sequence is used on PETN, there are four separate pulse sequences (two PAPS and two NPAPS). Between each of these sequences a relaxation delay is required to allow for the quadrupolar energy levels to return to equilibrium. Ideally, this relaxation delay should be at least equal to the spin-lattice relaxation time, T_1 , of the material. For PETN, the T_1 is 32 seconds, which gives a total PETN detection time (over RDX detection time) of about 96 seconds ($3 \times 32\text{s}$). Therefore, to obtain the same level of sensitivity from the standpoint of the detection sequence itself, a total time of about 106 seconds is required. However, by running the sequences consecutively, the time could potentially be reduced to about the same as that of the RDX sequence. For these reasons, it is likely that the detection sensitivity will be at least five times lower for PETN than for RDX-based explosives. In other words it will take at least 25 times more time to achieve the same sensitivity (because the signal-to-noise ratio increases as square root of the number of scans).

4.8 Nitrocellulose

Cellulose is a naturally occurring polymer of glucose and is usually found with over 3500 repeat units in a chain. Nitrocellulose is the nitrated form of cellulose, and is produced by reacting nitric and sulfuric acid with a variety of naturally-occurring cellulose materials. Nitration of the cellulose is never complete; however, an average of 12-14% N is common in explosive nitrocellulose. There are three potential nitration sites in a single cellulose monomer unit that are chemically non-equivalent. Even in "trinitrocellulose," the theoretical maximum nitration (14.1%) is not achieved. It is because of the slight changes in the local environment of the nitrogen caused by this partial nitration, combined with intramolecular interactions such as chain folding, that a large number of overlapping quadrupole transitions is likely to be seen in nitrocellulose. As can be seen from the case of relatively "crystallographically pure" TNT, this "dilution factor" causes a significant reduction in the potential for detection of quadrupole resonance transitions. As with the other nitro-group transition frequencies, the 14NO_3 is likely to be in the 500

to 1000 KHz range. An estimate of the best possible sensitivity of detection is shown in Table 1. This estimate is based on no dilution caused by partial nitration, intramolecular interactions and an estimated transition frequency of 1000 KHz. Some work has been carried out in analyzing the ^{14}N and ^{15}N wide-line NMR signals from nitrocellulose [20]. However, no information was obtained on the ^{14}N QR transition frequencies.

4.9 Stabilizers and Other Additives

The phenomenon of QR is restricted in substance detection to the investigation of crystalline solids. Amorphous materials, liquids and gases are not accessible to quadrupole resonance in this type of application. Implied is that stabilizers such as stearates, ethylene glycol, natural gums, and other liquid petroleum products commonly used in explosive mixtures are inaccessible to quadrupole resonance. There are a number of solid components found to a varying degree in explosive mixtures. In AN-based explosives, silicon dioxide is used as a water-proofing coat on the AN [23]. Unfortunately, silicon-29 (^{29}Si) is not a quadrupolar nucleus. Metallic aluminum is used as a stabilizer or sensitizer in some explosives. ^{27}Al , although quadrupolar, is not accessible in this form.

There are also a vast array of other less commonly used solid organic explosives that are all potentially accessible to QR detection, including organic azides, azines, perchlorates, hypochlorites, and peroxides. There is no currently available information on the QR characteristics of these materials, although most contain a significant percentage of nitrogen and/or chlorine.

Table 1. Estimated Relative QR Detectability of Some Explosives

Explosive Material	Quadrupolar Nucleus	Detection Frequency / KHz	Estimated Relative Sensitivity of Conventional (Faraday) Detection Compared to RDX 3410 KHz Resonance Transition*
RDX	^{14}N (ring)	3410	1.0
	^{14}N (ring)	1842	0.28
	$^{14}\text{NO}_3$	[1000]	0.16
HMX	^{14}N (ring)	3737	1.8
	^{14}N (ring)	1563	0.5
	$^{14}\text{NO}_3$	[1000]	0.25
TNT	$^{14}\text{NO}_3$	900	0.02
KNO_3	^{39}K	666	0.59
	$^{14}\text{NO}_3$	567	0.18
NH_4NO_3	$^{14}\text{NO}_3$	500	0.18
	$^{14}\text{NH}_4$	235	0.02
NH_4ClO_4	$^{35}\text{ClO}_4$	379	0.36
	$^{14}\text{NH}_4$	42	0.004
PETN	$^{14}\text{NO}_3$	890	0.19
Nitrocellulose	$^{14}\text{NO}_3$	[1000]	<<0.1

* Assuming identical relaxation times

[] Estimated Frequency

5 Conclusions

Plastic explosives are considered to present the most significant threat to airline security. The two major explosive constituents of plastic explosives are RDX and PETN. Fortunately, both these constituents are detectable by QR.

The detection of RDX in plastic explosives using QR has already proven feasible. This has been accomplished with laboratory systems using detection coils up to 300 liters in volume, as well as the first commercial package scanning system using detection coils up to 20 liters in volume. The pioneering work of the NRL and other groups have addressed most of the major technical difficulties arising from QR detection of RDX-based explosives in airline baggage.

PETN, although less readily detectable using QR techniques (and still undergoing characterization), poses perhaps the secondary biggest threat. Despite the fact that PETN takes at least five times as long to detect as RDX with conventional techniques (and possibly even longer), PETN should nevertheless be detectable in a reasonable scan time.

HMX is more readily detectable using QR than even RDX. However, the threat that HMX-based explosives pose to airline security is still a matter of some debate: no hard evidence exists either way. Our recommendations in the following section reflect this lack of information.

It is unlikely that conventional techniques will detect the other explosive materials discussed in this work with reasonable sensitivity. This is because conventional detection of quadrupole resonance signals relies on Faraday detection, which is inherently limited at frequencies below approximately 1000 KHz since sensitivity is based on the time derivative of the magnetic flux. Development of SQUID detection systems and techniques are likely to make the lower frequency responses of AN, AP, KNO_3 , and NC more readily accessible to QR detection applications. Moreover, detection of PETN using SQUID based detection may also be enhanced.

6 Recommendations

As it has already been established that plastic explosives present the greatest explosives threat to airline security, we recommend that the baggage screening technology developed under this contract be aimed at detecting the constituents of plastic explosives. Based on the findings of the recent work of the NRL group, the development of detection sequences combined with the threat posed by plastic explosives, we recommend that RDX and PETN—the two most common constituents of plastic explosives—be the target substances for the first commercial prototype QR explosives scanner.

A QR scanner capable of detecting HMX and RDX could equally well be developed. However, given the lack of information on the threat posed by HMX-based materials, our recommendation is a development of a QR scanner capable of detecting RDX- and PETN-based explosives.

Detection of the QR signals from PETN, TNT, AN, AP, KNO_3 , and NC will likely benefit from future advances made in SQUID-based detection systems and techniques. Moreover, because of the broad band nature of SQUID sensors, simultaneous detection of many explosives may be possible.

7 References

1. "Nuclear Quadrupole Resonance", T.P. Das and E.L. Hahn, Chapter in Solid State Physics, Suppl.1, Academic Press, New York, 1958.
2. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, 1961
3. "Steady State Free Precession in Nuclear Magnetic Resonance," H.Y. Carr, Physical Review, 112, 1693-1701, 1958.
4. "Nitrogen-14 NQR Study of Energetic Materials," R.A. Marino, R.F. Connors, and L. Leonard (Block Engineering), Final Report to on U.S. Army Research Office Contract DAAG29 79 C 0025, September 1982.
5. "Multiple Spin Echoes in Pure Quadrupole Resonance," R.A. Marino and S.M. Klainer, Journal of Chemical Physics, 67, 3388-3389, 1977.
6. "Explosives Detection by Pure ^{14}N NQR", A.N. Garroway, J.B. Miller and M.L. Buess, Proceedings of the 1st International Symposium on Explosive Detection Technology, November 13-15, 1991, Atlantic City, USA.
7. "Pulsed Spin Locking in Nuclear Quadrupole Resonance of ^{14}N ," D.Ya. Osokin, Soviet Physics. JETP, 57(1), 69-71, 1983.
8. "Experimental Investigations of the Strong Off-Resonant Comb (SORC) Pulse Sequence in ^{14}N NQR," S.S. Kim, J.R.P. Jayakody, and R.A. Marino, Zeitschrift für Naturforschung, 47a, 415-420, 1992.
9. "Pulsed Fourier Transform NQR of ^{14}N with a DC SQUID," M.D. Hurlimann, C.H. Pennington, N.Q. Fan, J. Clarke, A. Pines, and E.L. Hahn, Physical Review Letters, 69, 684-687, 1992.
10. "SQUID Technology for Improved NMR/NQR Measurements Below 1MHz," Quantum Magnetics, Final Report on NSF Award 9160966, September 29, 1992.
11. "Librational Motion of Hexahydro-1,3,5-trinitro-s-triazine Based on the Temperature Dependence of Nitrogen-14 Nuclear Quadrupole Resonance Spectra: The Relationship to Condensed-Phase Thermal Decomposition," R.J. Karpowicz and T.B. Brill, Journal of Physical Chemistry, 87, 2109-2112, 1983.
12. "Detection of Explosives by Nuclear Quadrupole Resonance (NQR)." A.N. Garroway, J.B. Miller, J.P. Yesinowski, and M.L. Buess, Naval Research Laboratory, Final Report on Contract NEODTC N0464A92WR04515, FAA DTFA03-83-A-00322, March 26 1993.

13. "Electronic Effects and Molecular Motion in β -Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine Based on ^{14}N Nuclear Quadrupole Resonance Spectroscopy," A.G.Landers, T.B.Brill, and R.A. Marino, Journal of Physical Chemistry, 85, 2618-2643, 1981.
14. "Nitrogen-14 Nuclear Quadrupole Resonance of Substituted Nitrobenzenes," S.N. Subbarao, E.G. Sauer, and P.J.Bray, Physics Letters, 42A, 461, 1973.
15. "Nitrogen-14 Nuclear Quadrupole Resonance Study of Substituted Nitrobenzenes," S.N. Subbarao and P.J.Bray, Journal of Chemical Physics, 67(9), 3947-55, 1977.
16. " ^{14}N and ^{39}K Nuclear Quadrupole Coupling in KNO_3 ," T.J. Barstow and S.N. Stewart, Zeitschrift fur Naturforschung, 45a, 459-463, 1990.
17. " ^{14}N NQR Study of the Structural Phase Transitions in NH_4NO_3 ," J.Seliger, V.Zagar, and R.Blin, Zeitschrift fur Physik B, Condensed Matter, 77, 439-443, 1989.
18. Private communication, R.A.Marino, Hunter College, CUNY, NY, September 1994.
19. "Nuclear Magnetic Resonance of ^{14}N and ^{35}Cl in Ammonium Perchlorate," T.J. Barstow and S.N. Stewart, Journal of Physics: Condensed Matter, 1, 4649-4657, 1989.
20. "Nitrogen-14 and Nitrogen-15 Wide-Line NMR Studies of Nitrocellulose," R.A. Marino, Final Technical Report for Task 7-09, Department of Army, 30 October 1987.
21. "Detection of NQR in Explosives," V.S. Grechishkin, Russian Journal of Physics, 35(7), English Pages 637-640, 1992. Translation of Izvestiya Vysshikh Uchebnyykh Zavedenii, Fizika, No.7, pp.62-65, July 1992.
22. Private Communication, T.J. Rayner, July 1994.
23. "Engineering Design Handbook: Explosives Series, Properties of Explosives of Military Interest," U.S. Army Materiel Command, January 1971.

Other Relevant QR Papers Not Referenced

1. "Detection of Explosives and Narcotics by Low Power Large Sample Volume Nuclear Quadrupole Resonance (NQR)", M.L. Buess, A.N. Garroway and J.B. Miller, U.S. Patent 5206592..
2. "Detection of Explosives by Nuclear Quadrupole Resonance," M.L. Buess, J.B. Miller, and A.N. Garroway, U.S. Patent 5233300.
3. "A Means for Removing Effects of Acoustic Ringing and Reducing the Temperature Effects in the Detection of Explosives and Narcotics by Nuclear Quadrupole Resonance," M.L. Buess, A.N. Garroway, and J.P. Yesinowski, Navy Case Number 74,325 (filed 30 Nov. 1992).
4. "Narcotics Detection using Nuclear Quadrupole Resonance," J. Shaw, Contraband and Cargo Inspection Technology International Symposium, Washington D.C., 28-30 October 1992.
5. "A Search for NQR Signals in Heroin and Cocaine," R.A. Marino and J.R.P. Jayakody, Final Technical Report on subcontract to Quantum Magnetics under US Customs contract TC-91-031.
6. "NQR for Bomb Detection: Solution to the Plastics Problem ?" D. Noble, Analytical Chemistry, 66 (5), 320A - 324A, March 1 1994.
7. "Explosives Detection by Nuclear Quadrupole Resonance (NQR)," A.N. Garroway, M.L. Buess, J.P. Yesinowski, J.B. Miller, and R.A. Krauss, Report on results of demonstration of prototype NQR explosives detector at FAA Technical Center in May 1994..
8. "NQR Device for Detecting Plastic Explosives, Mines, and Drugs," V.S. Grechishkin, Applied Physics, A55, 505-507, 1992.
9. "Short Range Remote NQR Measurements," T. Hirschfeld and S.M. Klainer, Journal of Molecular Structure, 58, 63-77, 1980.
10. "A Pulsed NQR-FFT Spectrometer for Nitrogen-14," J.C. Harding, D.A. Wade, R.A. Marino, E.G. Sauer, and S.M. Klainer, Journal of Magnetic Resonance, 36, 21-33, 1979.
11. "New Methods of Nuclear Quadrupole Resonance," V.S. Grechishkin and N. Ja. Sinjavsky, Zeitschrift fur Naturforschung, 45a, 559, 1990.